

and Rh atoms, which are separated by 5.579(2) Å. The n.m.r. spectra show that for (2) and (3) the hydridic hydrogen signals are displaced towards higher field and in the i.r. spectra  $\nu(\text{CO})$  is shifted towards higher frequencies. These data reflect significant modifications at the ruthenium atom.

The binuclear complexes were recovered unchanged after the catalytic reactions, indicating that the co-ordinated cyclo-octa-1.5-diene ligand is not altered. Because the Ru is co-ordinatively saturated, the creation of a co-ordination vacancy could well be necessary for catalysis. In this context the relatively long Ru-N(1) distance [2.283(5) Å] [N(1) is *trans* to the hydride ligand] suggests that this bond may be broken during the catalytic cycle.

Competitive catalytic experiments on hydrogen transfer

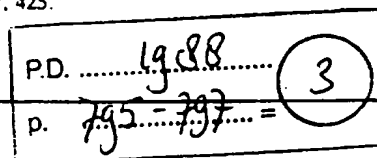
reduction of mixtures of cyclohexanone and styrene show preferential reduction of the carbon-oxygen double bond (Table 1). However, the  $\alpha,\beta$ -unsaturated ketone benzylideneacetophenone is preferentially reduced at the carbon-carbon double bond.

Received, 21st December 1987; Com. 1828

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XP-002095725



## Oxidative Cleavage of Carbon-Silicon Bonds by Dioxygen: Catalysis by a Flavin-Dihydronicotinamide Redox System

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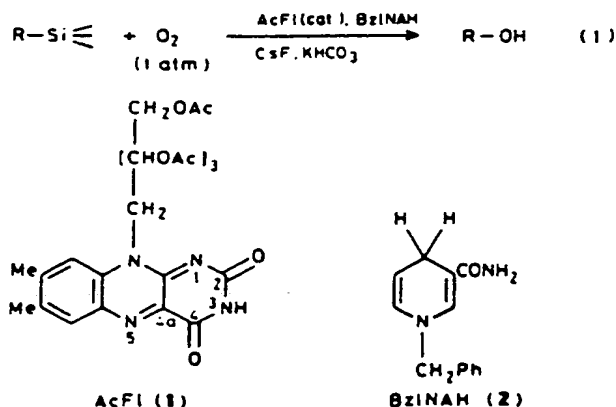
Carbon-silicon bonds in alkoxy- or fluoro-silanes readily undergo cleavage by dioxygen (molecular oxygen), catalysed by tetra-acetylriboflavin (5–10 mol %) in the presence of *N*-benzyl-1,4-dihydronicotinamide as reductant, together with fluoride ions as an essential additive.

A high resistance to oxidizing agents and towards aerobic oxidation is an outstanding property of organosilicon compounds, which have found a wide range of uses in the silicone industry.<sup>1</sup> However, we have recently reported the oxidative cleavage of certain carbon-silicon bonds<sup>2</sup> by hydrogen peroxide<sup>3</sup> and by peroxy acids;<sup>4</sup> these new oxidations are finding a variety of synthetic uses.<sup>5</sup> We now report an efficient cleavage of carbon-silicon bonds by dioxygen (molecular oxygen), catalysed by tetra-acetylriboflavin (AcFl) (1), in the presence of *N*-benzyl-1,4-dihydronicotinamide (BzNAH) (2) as reductant [equation (1)].

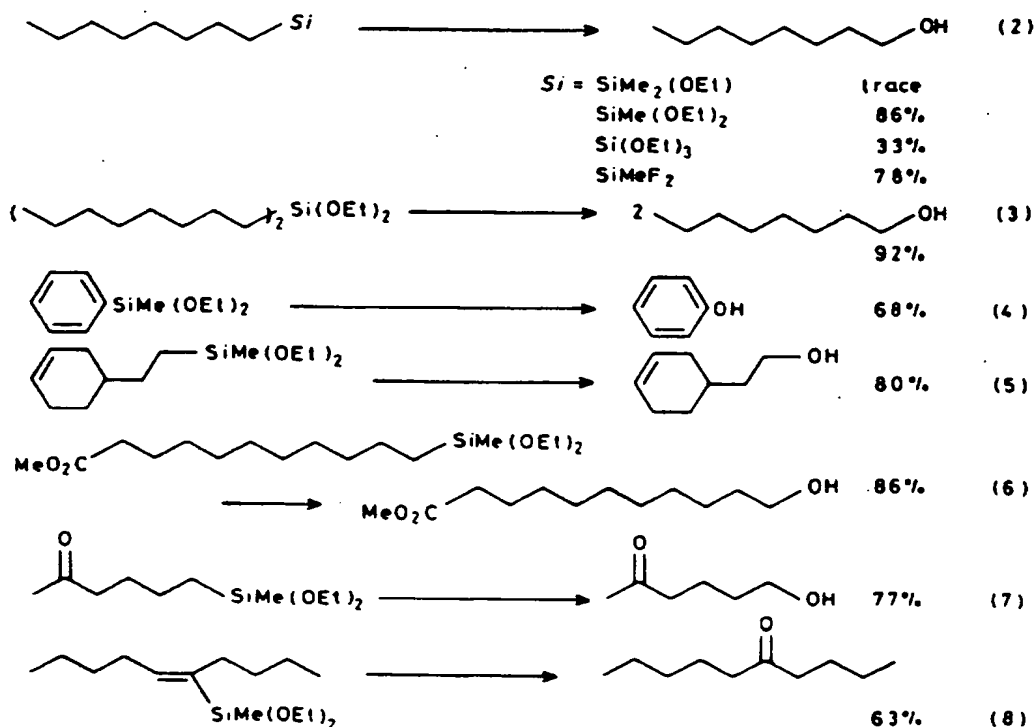
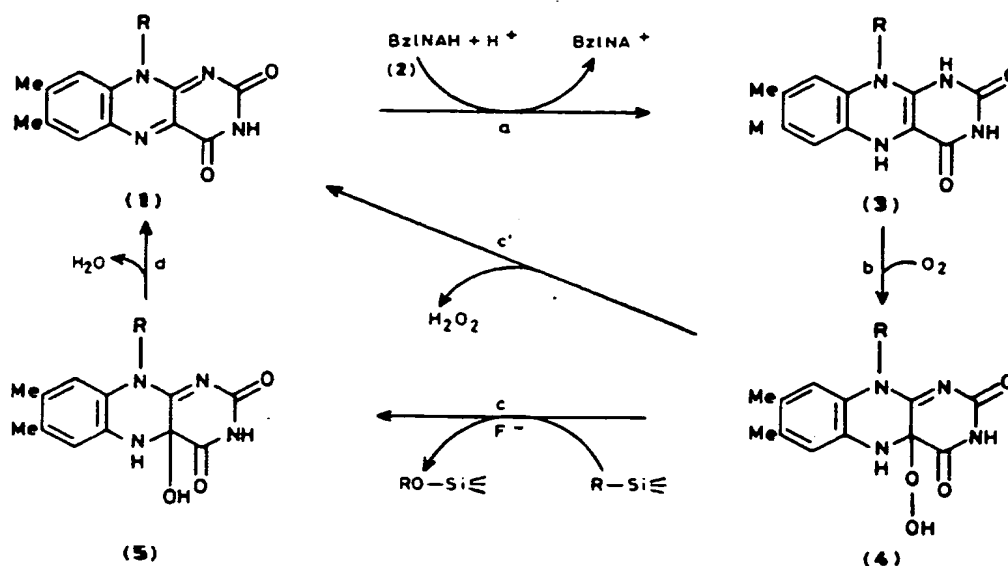
This represents the first application to organosilicon compounds of a biomimetic oxygenation system, based on enzymic flavin-dependent oxygen transfer, and analogous to the mono-oxygenases which catalyse epoxidation of alkenes, hydroxylation of hydroxybenzoates, oxygen transfer to sulphur and nitrogen compounds, and Baeyer-Villiger-type oxygenation of ketones.<sup>6,7</sup> It has been suggested that the key intermediates in these oxygenation reactions are 4a-hydroperoxyflavins (4), which tend to decompose to hydrogen peroxide and (1). The present oxygenation of carbon-silicon bonds may involve a similar catalytic cycle (Scheme 1). The organosilicon compounds may be oxidized by 4a-hydroperoxyflavin (4) (step c), or by  $\text{H}_2\text{O}_2$  generated in step c'. These steps require at least one functional group on silicon, and the presence of fluoride ions, as in our previous oxidations with hydrogen peroxide or peroxy acids.<sup>2–4</sup> The primary products (alkoxy-

silanes) may be hydrolysed to the corresponding alcohols by water produced in the catalytic cycle.

A typical experimental procedure is as follows. A mixture of diethoxy(methyl)(octyl)silane (1 mmol),  $\text{KHCO}_3$  (1 mmol), CsF (6 mmol), AcFl (1)<sup>†</sup> (0.1 mmol; 10 mol %), and BzNAH (2)<sup>†</sup> (4 mmol; 2 equiv. per Si-C bond) in 1:1 dry tetrahydro-



<sup>†</sup> Acetylation of riboflavin was accelerated by addition of 4-dimethylaminopyridine as a catalyst.



furan (THF)–dry ethanol (50 ml) (making a  $2 \times 10^{-2}$  M solution) was stirred at  $50^\circ\text{C}$  in the dark under 1 atm of dioxygen (balloon). After several hours, more BzI2NAH (1 equiv.) was added, and the mixture was stirred for a total of 10–20 h. The starting silicon compound had then disappeared completely (g.l.c.). Solvents were evaporated off and the brown tarry residue was diluted with ether and filtered. The filtrate was evaporated and the residue subjected to column chromatography [silica gel; hexane–ethyl acetate (5:1)] to give pure octan-1-ol in 86% yield (of isolated material).

The oxidation was dependent upon several factors, as observed with  $(n\text{-C}_8\text{H}_{17})\text{SiMe}(\text{OEt})_2$  as model substrate: the yields (g.l.c.) of octanol given refer to the standard conditions, unless otherwise stated. (i) The amount of catalyst (1) may be reduced to 5 mol % (75% yield), but 1 mol % is not sufficient (<20% yield). (ii) The presence of fluoride ion (CsF, not KF) is essential (2 equiv., 62%; 1 equiv., 36%; 0.5 equiv., 9% yield). In the absence of CsF no oxidation occurs; starting material is unchanged. (iii) The oxidation may be achieved in air instead of pure dioxygen: 5 mol % f (1), 18 h, 64% yield.

(iv) The concentration of the substrate may also be important. With a  $5 \times 10^{-2}$  M solution lower yields (55%) were obtained. This may be related to the total amount of dioxygen dissolved in the reaction mixture.† (v) The oxidation proceeds at lower temperatures, but slowly (at 25 °C for 3 h, 17%; for 23 h, 58% yield).

Results obtained under the standard conditions are summarized in equations (2)–(8). A dialkoxy silicon compound was more reactive than a monoalkoxy analogue [equation (2)]; the latter was recovered, but reacted in DMF<sup>3,4</sup> to form octan-1-ol in 66% yield after 15 h. A dialkyl silicon compound is converted into the alcohol [equation (3)]. A phenyl derivative gives phenol [equation (4)]. Several functional groups are unaffected by the oxidation. In particular, oxidative cleavage of carbon–silicon bonds leaves intact alkene and ketone functionalities [equations (5) and (7)], which might be expected to undergo epoxidation<sup>7b</sup> or Baeyer–Villiger oxidation.<sup>7a</sup> Alkylsilanes thus can be oxidized to the corresponding ketones without formation of esters [equation (8)].

This simple oxidative cleavage of carbon–silicon bonds by dioxygen catalysed by a biomimetic redox system should be of synthetic and mechanistic interest. The present results might throw light on problems concerning the decomposition pathways of organosilicon compounds in the environment and their non-existence in nature.<sup>11</sup>

Received, 29th January 1988; Com. 8/00319J

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† Solubility of O<sub>2</sub> (mol fraction):  $5.635 \times 10^{-4}$  at 323.15 K in EtOH;  $8.16 \times 10^{-4}$  at 298.15 K in THF.<sup>10</sup>

## Methane Adsorption on a Working Samarium Oxide Catalyst and its Role in Hydrocarbon Formation during High Temperature Partial Oxidation

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Although methane is strongly adsorbed on a samarium oxide catalyst at 700 °C, the adsorbed form does not participate directly in the formation of the hydrocarbon products of the partial oxidation reaction.

The catalysed reaction of methane with oxygen to form higher hydrocarbons represents an intriguing mechanistic problem. Ito *et al.*<sup>1</sup> first observed this reaction using a Li-doped MgO catalyst, and suggested that it involved the production of 'CH<sub>3</sub>' radicals on Li<sup>+</sup>O<sup>2-</sup> sites, which formed ethane by gas-phase dimerisation. This observation has been extended to a variety of catalysts, some of which (e.g. samarium oxide)<sup>2</sup> are much more active than Li-MgO and which obviously cannot contain these particular centres. Recently, carbene has been sugges-

ted as an intermediate in the reaction,<sup>3</sup> but the observation of a CH<sub>3</sub>/CD<sub>4</sub> isotope effect for the product formation has again been cited<sup>4</sup> as supporting the involvement of methyl radicals.

A crucial step in the determination of any catalytic mechanism is the estimation of the extent of adsorption and, if possible, the nature of the adsorbed reactants. Isotope switching techniques, in which one labelled reactant replaces the normal species without disturbing the steady state of the reaction, are effective in obtaining such data.<sup>5</sup> We have used

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